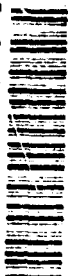


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CRDEC-TR-333

**SAFE REPLACEMENT MATERIALS FOR DOP
IN "HOT SMOKE" AEROSOL PENETROMETER MACHINES**

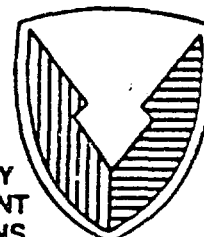
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**Hugh R. Carlon, U.S. Army Fellow
Mark A. Guelta**

RESEARCH DIRECTORATE

March 1992

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**U.S. ARMY
ARMAMENT
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13. ABSTRACT (Maximum 200 words) For many decades dioctyl phthalate (DOP), a common industrial material, has been used by the U.S. Army and other agencies to simulate aerosol behavior in non-destructive gas mask and filter serviceability testing, and for related test purposes. Techniques are completely standardized. But DOP has been labeled a hazardous material. The research reported here, which was performed using ATI Q-127 and TDA-100 "hot smoke" aerosol penetrometer test machines, identified relatively innocuous, inexpensive replacement materials for DOP. One of these, a synthetic hydrocarbon (poly alpha olefin (PAO)), can be used to replace DOP directly with minimum impact upon existing hardware and procedures. Of more than two dozen candidate replacement materials that were tested, isostearic acid and oleic acid also performed well as DOP replacements. All three materials also show promise for cold smoke testing applications.					
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PREFACE

The work described in this report was authorized under Engineering Study Proposal (ESP) No. FI-7-8860, "Alternative for DOP," and was completed using OMA funds under in-house Project No. FI-7-8860. This work was started in September 1987 and completed in June 1991.

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SAFE REPLACEMENT MATERIALS FOR DOP IN "HOT SMOKE" AEROSOL PERMETRONETER MACHINES

1. INTRODUCTION

Di (2-ethylhexyl) phthalate, also called dioctyl phthalate, di-sec octyl phthalate, DOP, or DEHP, is a widely used industrial material. Over ninety percent of the material produced is used as a plasticizer, primarily for PVC plastics. The properties of DOP that make it useful as a plasticizer, including low vapor pressure, chemical stability, and insolubility in water, also make it useful as a test aerosol. DOP aerosols are used in respirator fit testing, HEPA filter testing, aerosol research, aerosol instrument calibration, and other applications. These uses involve human occupational exposure to submicrometer-sized DOP aerosols, often briefly but in moderately high concentrations.¹

Concern about the potential health effects to people working with DOP test aerosols has led to a search for substitute materials.¹ This search has taken a number of different directions, depending in part upon the specific test applications for which a DOP replacement has been sought. For example, Hinds, et al.,² looked at size distributions of test aerosols of corn oil, di (2-ethylhexyl) sebacate (DOS), mineral oil, and polyethylene glycol (PEG), and compared these to DOP. Gerber³ has published a detailed study of glycols as safe DOP replacements. Other comparative studies of size distribution and filter penetration of corn oil,⁴ mineral oil, PEG, and DOP have been reported.⁵ Interest has been revived in the use of solid aerosols including salts as test media,⁶ and their performance compared to DOP aerosols.

The U.S. Army routinely performs 100% quality control testing of filter canisters manufactured for use with field-issue gas masks, and periodic sampling and testing of canisters stored in its supply depots. In April, 1986, the U.S. Army Surgeon General placed severe restrictions upon testing with DOP; agencies were also informed that dioctyl sebacate (DOS) would no longer be acceptable as a DOP replacement material, and that similar restrictions would apply for both. These restrictions included occupational exposure monitoring of workers exposed to DOP aerosols and liquid, medical surveillance, issue of personal protective equipment, formal notification to workers of associated risks, and labeling of work areas as "cancer suspect agent areas."

Clearly, these actions placed severe restrictions upon routine, 100% quality assurance testing of filters and other equipment. For this reason, in 1988 the U.S. Army initiated a detailed study of the problem of finding an acceptable substitute material for DOP that could meet all standard military test specifications while itself being a non-carcinogen and, ideally, having other attributes including acceptable acute inhalation toxicity, low cost, ready availability, and the ability to replace DOP directly in machines at test installations without retrofit or other modification of these machines.

This paper describes the experimental procedures and results of that study which are applicable primarily to "hot smoke" aerosol penetrometer machines including the Army-standard "Q-127" machine that is currently produced as the Model TDA-100 by Air Techniques, Inc. (ATI).⁷ Several dozen samples of promising materials were obtained and tested in two filter-penetrometer machines: (1) a standard Q-127 "hot smoke" machine, and (2) the Los Alamos Monodispersed Aerosol Prototype Penetrometer (LAMAPP), a state-of-the-art developmental machine that produces smokes from liquids at room temperature. The two most promising materials were later tested in two brand new TDA-100 machines and compared with DOP smokes from a third brand new TDA-100 machine at the factory, by invitation of the manufacturer, ATI.

While this paper will discuss briefly the testing carried out and results obtained with both kinds of penetrometer machines, it will concentrate most upon "hot smoke" technology. Replacement materials for "cold smoke" applications will be discussed fully in a later paper.

2. TEST SMOKE SPECIFICATIONS

Present U.S. Army test specifications for acceptable "hot smokes" prescribe a geometric mean diameter (GMD) of between 0.18 μm and 0.33 μm , with a geometric standard deviation (GSD) equal to or less than 1.30, and a mass concentration at the test chuck, where filters are held for penetration measurements, of $100 \pm 20 \text{ mg}/\text{m}^3$. The mass concentration of an aerosol in milligrams per cubic meter is given by the equation:

$$\text{mg}/\text{m}^3 = \frac{\pi}{6} \times 10^{-3} d N D_{\mu\text{m}}^3 \quad (1)$$

where d is the density of the material, N is the aerosol particle population per cubic centimeter, and $D_{\mu\text{m}}$ is the particle diameter in micrometers. In Figure 1, Equation 1 is plotted for unit density spheres for three values of the GMD. It is seen that as the aerosol mass concentration approaches $100 \text{ mg}/\text{m}^3$, the number of 0.3 μm particles per cubic centimeter approaches 7×10^6 , and that this number for 0.2 μm particles is well in excess of 10^7 .

UNIT DENSITY SPHERES

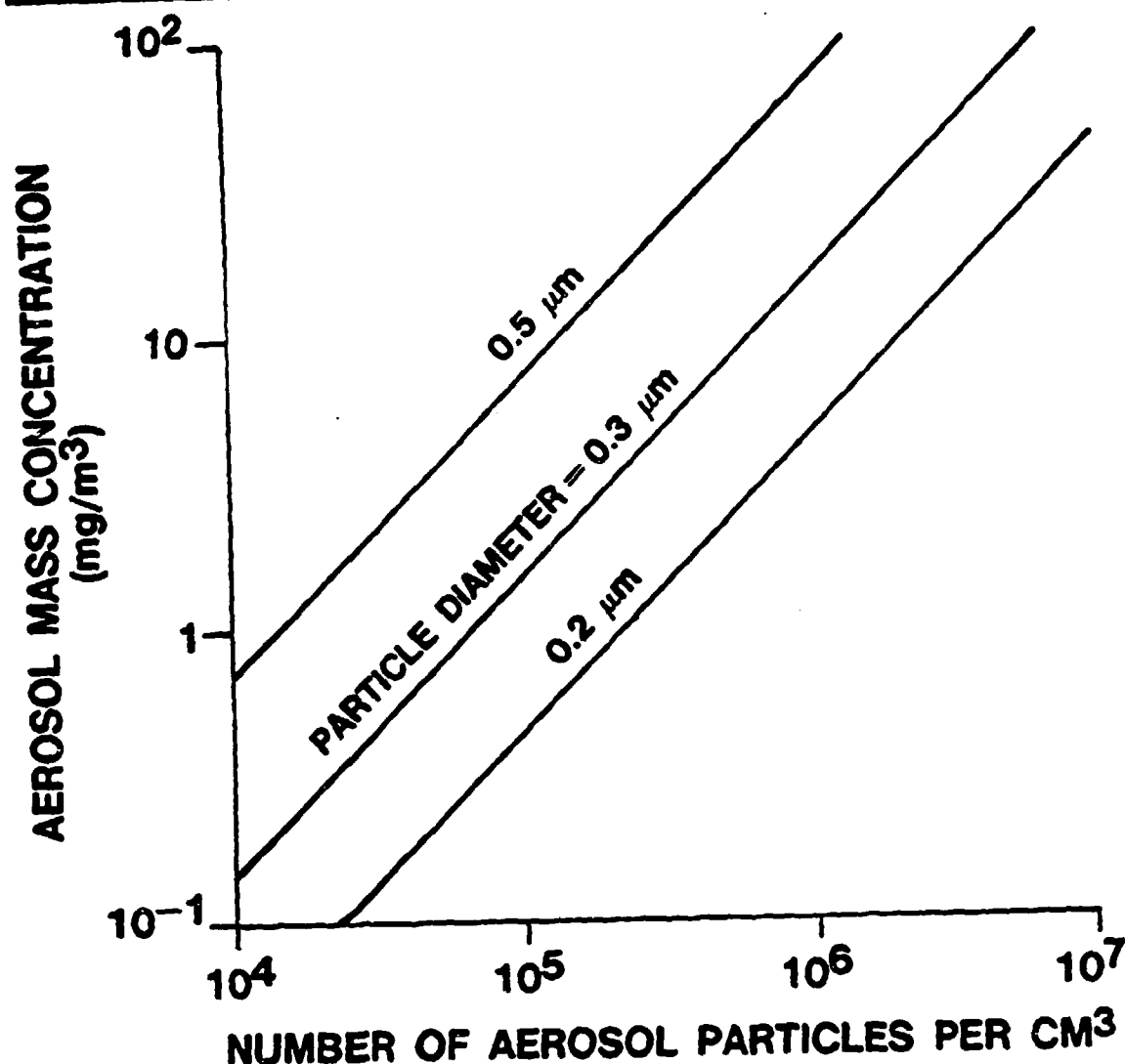


Figure 1. Plot of Equation 1 for Unit Density Spheres

Populations as large as these exceed the operating ranges of laser aerosol spectrometers like the one discussed below that was used in our studies. Typically, these instruments can count 1.7×10^4 particles with 90% accuracy in a one cubic centimeter sample per second. Thus an accurate aerosol dilution of several hundred times is required to count the particles delivered to a Q-127 machine canister test chuck at 100 mg/m^3 . In the research reported here, such aerosol dilutions were made routinely using precision equipment.

Our Q-127 machine was a refurbished older model of the similar but redesigned and simplified "monodispersed aerosol penetrometer" presently being marketed by ATI under the model number TDA-100.⁷ These machines generate "hot smokes" by the vaporization and recondensation of DOP or other liquids, having suitable vapor pressure and other physical properties, which are placed in a heated reservoir. Hinds, et al,⁸ described "hot DOP" aerosol size distributions produced by the ATI Q-127 machine more than a decade ago, and gave a good description of changes in aerosol output corresponding to various settings of the mechanical analyzer (modified nephelometer) or "Owl" that is standard equipment on all Q-127s and TDA-100s. They found that the output aerosol could be varied over the GMD range 0.23-0.30 μm corresponding to angular range 0.23-0.30 μm corresponding to angular settings of the Owl from 29° to settings of the Owl from 29° to 45°, respectively. These results can be compared to ours, which are reported below.

A PMS Model LAS-X laser aerosol spectrometer⁹ was used in our research to measure GMD of test aerosols in four diameter ranges between 0.09 μm and 3.00 μm . Fifteen channels of size resolution were provided in each range. (Hinds, et al,⁸ used a PMS Model ASASP-300 aerosol spectrometer; Skaats¹⁰ performed similar DOP studies using an LAS-200 laser aerosol spectrometer in tests to Army specifications with Q-127, Q-107, and Q-76 machines). We used precision gas diluters to prepare samples for size measurement from the Q-127, which were drawn from the analyzer (Owl) chamber, for introduction directly into the LAS-X system.

The LAMAPP system is shown in Figure 2. It is described in greater detail in Ref. 12. A fine polydisperse aerosol is generated by a Laskin nozzle in a "cold pot" containing the test liquid. In a similar pot containing an NaCl solution, droplets are produced that evaporate to form salt condensation nuclei as they flow through a vaporization tube, where the DOP or other liquid aerosol is simultaneously vaporized. Upon cooling, the liquid recondenses on the salt nuclei to form droplets of controlled size and small GSD. These enter an aging chamber from which they are drawn for filter test purposes. Provision is made for calibration using polystyrene latex (PSL) or other standard aerosols. A laser aerosol spectrometer (LAS-X) and microcomputer permit GMD and GSD to be determined and printed on a strip chart.

Toxicological properties of candidate materials were of paramount importance in our study. Classes or families of materials known to be non-carcinogenic and relatively non-toxic were required to be screened for possible candidates which, at the same time, had physical properties such that they might produce acceptable aerosols in the penetrometer machines. And, ideally, they should offer other inducements to their use such as low cost.

Material Safety Data Sheets (MSDS) were compiled for promising materials, which included straight-chain saturated hydrocarbons (cosanes), moderately branched-chain saturated hydrocarbons, fatty acids, fatty acid esters, and glycols. The MSDS indicated that virtually all of these materials were classed as having very low toxicity to humans. Many, in fact, were approved for use in foods and cosmetics. But virtually no data were found to exist concerning the inhalation toxicity to humans of these materials when breathed as fine aerosols or smokes.

"MONODISPERSE" AEROSOL PENETROMETER ("LAMAPP")

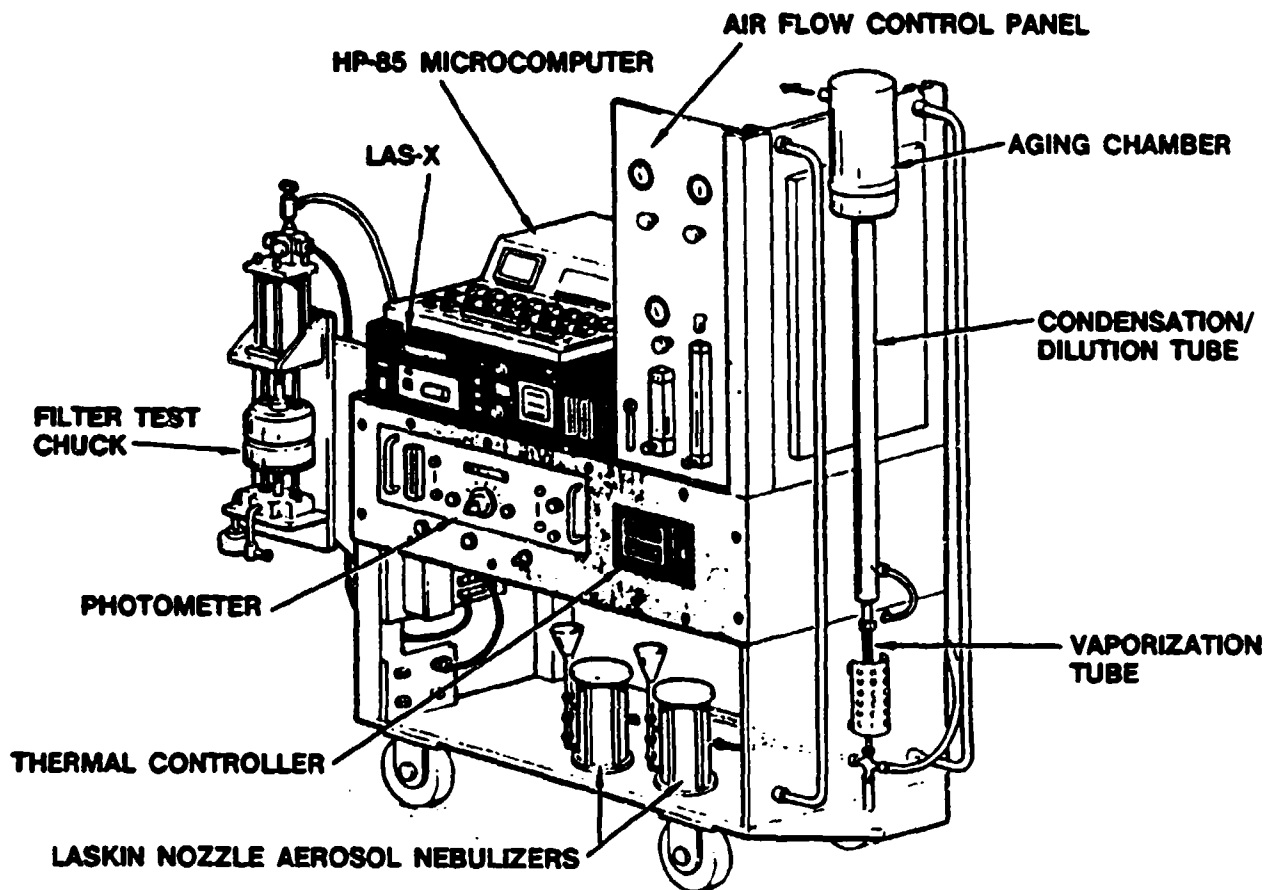


Figure 2. LAMAPP System

The U.S. Army Chemical Research, Development and Engineering Center (CRDEC) has developed computerized data bases of many chemical compounds that can be searched for toxicological and physical properties. Search routines were executed to determine which compounds from the classes of materials mentioned above were in these data bases. These materials were in turn searched to optimize matches of physical properties that were thought to be important in aerosol generation by vaporization/recondensation processes.

3. SELECTION AND TESTING OF CANDIDATE MATERIALS

Several candidate replacement materials for DOP were identified on the basis of presumed inherent low toxicity. The approach was two-fold: (1) to find those materials that might work best in the machines, considering reproducible particle size, size distribution, smoke concentration, market availability, and cost; (2) to subject those materials to replacement testing in production and/or product assurance penetrometer machines, and seek final approval for the use of any successful material(s) to replace DOP.

Other factors which must be considered in choosing a material to replace DOP are: (1) the impact of a new material upon existing testing hardware must be minimal; (2) machine maintenance- it is undesirable to use a material that will clog the testers and/or will support fungus growth; (3) destructive vs. non-destructive testing- DOP penetration testing is considered non-destructive, and a new material must also be non-destructive in the sense that it will not damage filters in standard test aerosol concentrations (even DOP might damage filters in massive concentrations); (4) a new material must exhibit adequate stability and aging characteristics, especially at elevated reservoir temperatures found in Q-127 and TDA-100 machines.

Many physical properties appear to play some role in the behavior of candidate materials when they are used in filter penetrometer machines such as the Q-127. Among these physical properties are vapor pressure, surface tension, viscosity, and density.

Figure 3 presents a Clausius-Clapeyron plot for several potential candidate materials, relating the logarithm of vapor pressure to the reciprocal of absolute temperature in degrees Kelvin. The upper scale on the abscissa also gives temperature in degrees Celsius. The negative slope of the curve for each material corresponds to its heat of vaporization divided by the gas constant. Such curves are readily constructed if vapor pressures for a given material are known at two or more temperatures.

In Figure 3, it can be seen that the curve for DOP lies below the others, indicating that DOP has a lower vapor pressure at a given temperature than the other materials shown. As the molecular weight increases in a family of candidate chemical compounds, the vapor pressure decreases. Thus as the carbon chain length in capric, lauric and myristic acids increases from C = 10 to 12 to 14, respectively, the curves in Figure 3 for these acids approach the lower curve for DOP.

This simple analysis suggests that as the fatty acid carbon chain length increases a better match is made with the vapor pressure characteristics of DOP. Thus palmitic acid (C = 16) or stearic acid (C = 18), which are not shown in Figure 3, should most closely match DOP in this respect. But the fatty acids just discussed are all solids at room temperature; their melting points range from 31°C for capric acid to 68°C for stearic acid. As their vapor pressure characteristics become more like those of DOP, they become increasingly difficult to work with. They will melt in the Q-127 machine pot and will vaporize, but the recondensation aerosols that they produce will become increasingly unpredictable with increasing chain length and melting point.

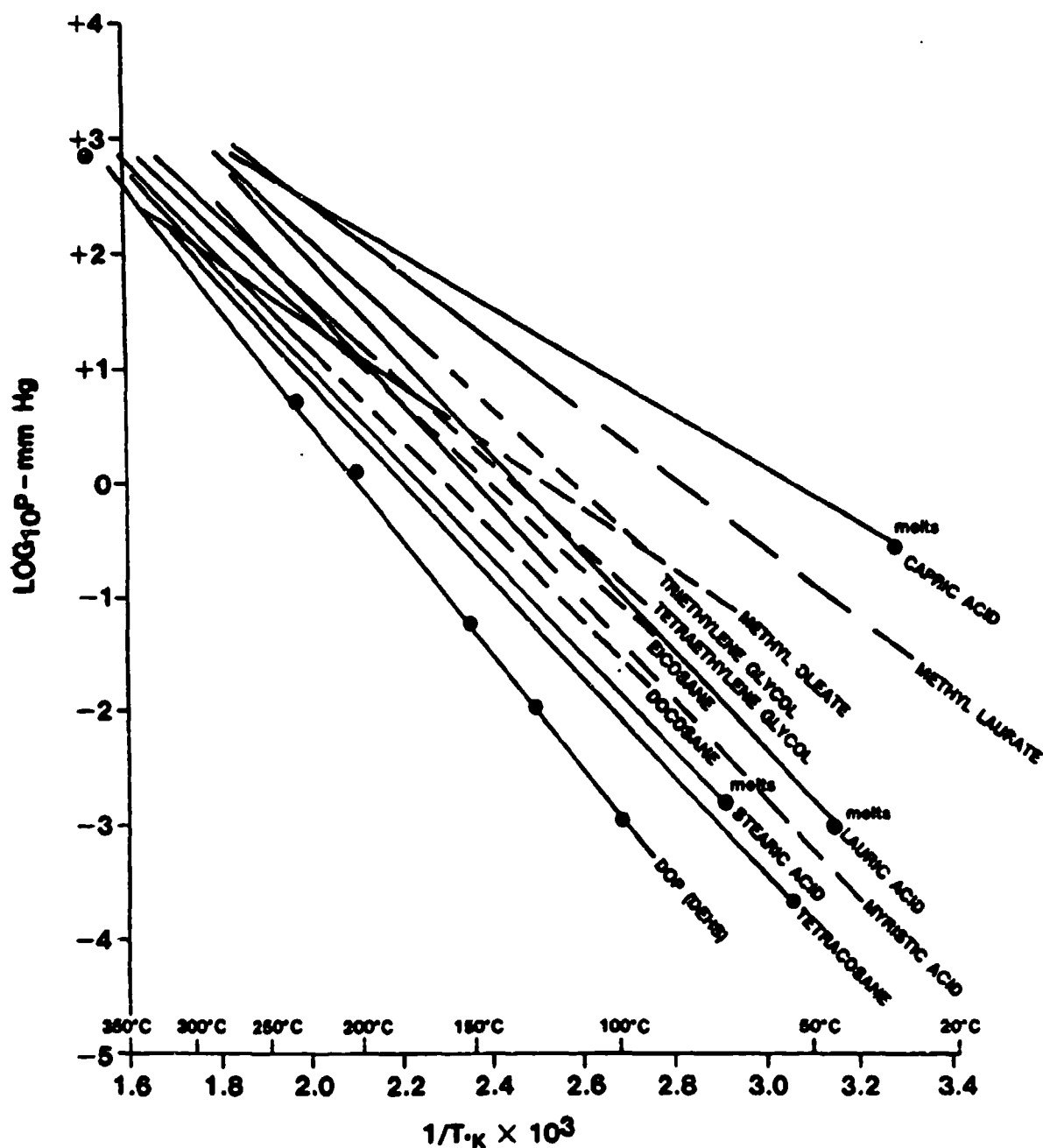


Figure 3. Clausius-Clapeyron Plot; DOP and Some Candidate Replacement Materials

It is much easier to work with candidate materials that are liquids at room temperature. But such materials usually have two characteristics that are undesirable: (1) they are unsaturated; i.e., they contain C:C double bonds that are sites for chemical attack leading to instability with aging, especially at elevated temperatures, and thus rancidity and fungus growth could result; (2) their carbon chains are branched, rather than straight as for the fatty acids just discussed, and this increasingly complex structure increases the probability that human toxicological problems will be encountered in their use.

Figure 3 suggests how compromises might be made to find a simulant for DOP to use in the Q-127 machine. Suppose, for example, that the Q-127 machine pot is normally maintained at 150°C (shown on the upper abscissa scale in Figure 3) when it contains DOP. This corresponds to an ordinate value of -1.3, or a DOP vapor pressure of 0.050 mm Hg. Moving horizontally to the right at the -1.3 ordinate value, we encounter the myristic acid curve at a temperature of about 100°C. This indicates that we should obtain the same vapor pressure with myristic acid at a pot temperature of about 100°C that we would obtain with DOP at 150°C.

There are other complications. For example, the Q-127 machine pot temperature might not be conveniently adjusted to a temperature as low as 100°C. Even if this were possible, the acid might not recondense into an aerosol under conditions achievable using other Q-127 machine settings, or it might not yield an aerosol with the proper specifications. Even if the acid were to perform well, it would still freeze during shut-down in the Q-127 machine pot and fittings, because its melting point is 52°C. Its inhalation toxicological properties would still remain to be investigated.

Our Q-127 and LAMAPP penetrometer machines were supplied by air from a compressor. The inlet air line was fitted with a refrigerative dehumidifier to remove moisture and other contamination, such as oil, from the air supply.

The machines were provided with two precision capillary air diluters in series to sample aerosols for analysis by the LAS-X laser aerosol spectrometer. Each air diluter was adjustable for dilution ratios up to 100:1 (10,000:1 maximum in series) at flow rates up to 5 standard lpm. Each diluter employed a closed system using filtered air from the original sample to mix with and reduce the concentration of the aerosol at the output. The dilution air passed through two in-line high-efficiency particulate aerosol (HEPA) filters.

LAS-X data for the Q-127 machine were compared directly with readings from the optical "Owl" device on the Q-127 machine which was set to a given angular reading (usually 29°) corresponding to a "standard" DOP test aerosol. In this way, Q-127 machine operators could be instructed as to which control settings should be used to obtain proper test aerosols from DOP replacement materials, since they would not normally have access to a LAS-X system in filter quality testing.

A detailed Standing Operating Procedure (SOP) was prepared to permit safe machine operation with DOP, as well as with candidate replacement materials. Candidate samples were aged in an oven at 140°C concurrently with their use in the penetrometer machines. In this way the stability and aging characteristics of promising candidate materials could be studied over periods ranging from weeks to months, even though their time of use in the machines would be limited to days because of the pressing schedule of candidate material testing.

A discussion of Q-127/TDA-100 and LAMAPP operating adjustments and procedures is beyond the scope of this brief discussion. Some information is contained in a paper submitted to the AAAR journal.¹¹ Complete details are contained in a CRDEC report that has been cleared for public release; a copy is available upon request from the authors.¹²

In summary, the required performance criteria for candidate materials to successfully replace DOP are clear: they must be toxicologically and environmentally innocuous when dispersed as aerosols, and they must have physical and chemical properties sufficiently similar to those of DOP to allow them to produce aerosols like those of DOP when subjected to evaporation and recondensation in filter penetrometer testers such as TDA-100 and Q-127 machines. Ideally, they should also work in machines that operate at room temperature.

About three dozen candidate materials were obtained from several suppliers including the primary manufacturers.¹³ These materials were either liquids or solids at room temperature. A test priority was established such that the materials were evaluated in the sequence: (1) liquids in the Q-127 machine; (2) solids in the Q-127 machine, in order of increasing melting point; (3) liquids in the LAMAPP machine.

Our experiments identified several materials that are viable candidates to replace DOP in "hot smoke" penetrometer machines such as the Q-127/TDA-100, and in "cold pot" machines like LAMAPP. These are summarized in Table 1, with sources of supply.¹³ The materials identified here as DOP alternatives or replacements are generally inexpensive, and readily available. Aging tests at elevated temperatures, which are presently underway, should identify candidate materials that are thermally unstable.

Most candidates should be quite stable in long-term testing, if not contaminated in use. Indeed, some candidate materials that contain significant percentages of "impurities" (compounds similar to the primary compound, but more volatile) actually seem to improve in performance with aging at elevated temperatures.

4. DISCUSSION

Isostearic acid has the structural formula:



where the single branched methyl group usually occurs in the position shown but also can occur at any other position along the carbon chain with a much lower probability. Thus it is an isomer of stearic acid, but the two acids have distinctly different physical properties. Isostearic acid is a light yellow liquid at room temperature with a melting point of 12-15°C, depending upon its purity, and it has a vapor pressure of 50 mm Hg at 285°C. Its flash point is approximately 182°C, open cup.

Two samples of differing purity were used in this work. The purest sample was 70-76% isostearic acid, with the remainder consisting of myristic, isopalmitic, and palmitic acids, in that order. The less pure sample was 40-66% isostearic acid, with the remainder consisting of isooleic, oleic, stearic, and isopalmitic acids, in that order.

Both samples worked very well in our Q-127 machine, with the purer material yielding slightly higher aerosol concentrations. The purer material also worked very well in the LAMAPP machine. This can be observed in Table 1.

Table 1. Recommended Replacement Materials for DOP in Q-127 and TDA-100 Machines, and in the LAMAPP Machine, Ranked in Order of Probable Success

Ranking*	Q-127 and TDA-100 Machines		LAMAPP Machine	
	Chemical Name	Manufacturer ⁽¹³⁾ or Source	Chemical Name	Manufacturer ⁽¹³⁾ or Source
1	synthetic hydrocarbon Emery 3004	Emery Group Henkel Corp..	synthetic hydrocarbon Emery 3002	Emery Group Henkel Corp.
2	isostearic acid (76%) Emersol 875	Emery Group Henkel Corp.	isostearic acid (76%) Emersol 875	Emery Group Henkel Corp.
3	isostearic acid (66%) Emersol 871	Emery Group Henkel Corp.	methyl oleate stearate Emery 2219	Emery Group Henkel Corp.
4	synthetic hydrocarbon Emery 3006	Emery Group Henkel Corp.	synthetic hydrocarbon Emery 3004	Emery Group Henkel Corp.
5	oleic acid (71%) Industrene 206LP	Hunko Chem. Div., Witco Chem. Corp.		
6	oleic acid (74%) Emersol 233LL	Emery Group Henkel Corp.		

* Highest rankings have highest probability of success.

The oxidation stability of isostearic acid appears good compared to other candidate materials. A weak acid, isostearic acid is not recommended for use in contact with chemically-active metals such as brass and iron, especially at elevated temperatures. Stainless steel, or other inert materials should be specified for the fabrication of the "hot pot", e.g., on TDA-100 machines, if isostearic acid were to be used owing to its other desirable properties. For this reason a synthetic hydrocarbon, described below, was given first priority for use in hot smoke machines, as is shown in Table 1.

Synthetic hydrocarbons include poly-alpha olefins (PAOs), which are used as synthetic lubricants, and in other applications. These versatile, saturated, synthetic hydrocarbons are produced by direct oligomerization of decene-1. Linear alpha olefins are polymerized and hydrogenated to manufacture PAOs. Three PAOs were investigated in our studies; these are designated Emery 3002, 3004 and 3006. Data are summarized in Table 2.

Table 2. Properties of Poly-Alpha Olefins (PAOs)

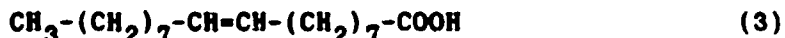
Trade Name	Pour Point, °C	Flash Point, °C	Fire Point, °C	Auto-Ignition Point, °C	Specific Gravity
Emery 3002	-65	164	178	324	0.80
Emery 3004	-69	225	250	343	0.82
Emery 3006	-64	243	266	371	0.83

See Ref. 13

In the Q-127 machine, Emery 3004 performed best, giving a GMD adjustable from 0.2 to 0.3 μm , with a GSD of 1.23 and an adequate aerosol yield. The "pot" temperature was 180°C. Emery 3002 was too volatile, and produced large aerosol yields that could not be adjusted to GMDs below 0.3 μm , and which had GSD values of 1.40-1.67 or more. Emery 3006 had to be heated to 195°C to yield 110 mg/m^3 of aerosol with a GSD value of 1.20, but the GMD could not be adjusted above 0.21 μm .

Emery 3002 performed well in the LAMAPP machine, giving smokes with specifications as good as those for Emery 3004 in our Q-127 machine, and thus it was given first priority for use in the LAMAPP, compared to fourth priority for Emery 3004 in that machine.

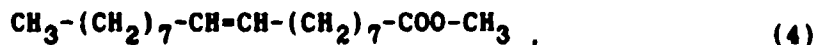
Oleic acid has the structural formula:



where one double bond exists between the ninth and tenth carbons of an 18-carbon chain. The molecule is most easily chemically attacked at this double bond, making this acid less stable during aging at elevated temperatures than saturated fatty acids. Nevertheless, it performs well in the Q-127 machine with the exception that the aerosol concentration is so great that it is sometimes difficult to control. Oleic acid is not recommended for use in the LAMAPP machine.

The oleic acid used here was 71-74% pure, with the remainder consisting mainly of palmitoleic and linoleic acids, in that order. It is a light yellow liquid at room temperature, with a slight odor. It melts at 11-14°C, and has a vapor pressure of 10 mm Hg at 224°C. Its flash point is approximately 184-189°C closed cup, and 193°C open cup.

Methyl oleate stearate is a mixture of 58% methyl oleate, whose structural formula is:



24% methyl stearate, whose structural formula (where $n = 18$) is:



14% methyl linoleate, and 4% methyl palmitate ($n = 16$ in the formula above). It melts at 18°C , and is a light yellow liquid. Its vapor pressure is 10 mm Hg at 205°C , and its flash point is approximately 173°C open cup.

This material produced a thin smoke in the Q-127 machine that could not be read by the Owl. The GMD range was 0.24-1.1 μm , and the GSD range was 1.40-1.50. However, the material performed well in the LAMAPP machine, for which it was given third priority for use as indicated in Table 1.

Our primary mission in this program was to identify a safe replacement material for hot smoke machines including Q-127/TDA-100s that could be used to replace DOP directly in existing machines with a minimum of downtime and/or machine modification. That best material (Emery 3004) would then have to pass toxicological screening so as to, ultimately, obtain approval by the U.S. Army Surgeon General for use Army-wide. The remainder of this paper thus concerns itself with hot smoke machines; the LAMAPP will receive little further attention here but is considered in detail elsewhere.¹²

We were invited by the management of Air Techniques, Inc.⁷ to carry out comparative testing of DOP and our two best candidate replacement materials in three brand-new TDA-100 (formerly Q-127) penetrometer machines on their production line, during "break-in" in the early months of 1990. Data obtained from these tests were extremely valuable.

The materials selected for comparison with DOP were Emersol 875 isostearic acid, and Emery 3004 synthetic hydrocabron (poly alpha olefin, or "PAO"). The reservoir ("hot pot") of each machine was filled with one of the three materials.

The machines were adjusted to give smoke yields at the test chucks of 100 mg/m^3 , in accordance with Army specifications. The DOP machine was adjusted according to ATI specifications for new machines, and the machines containing isostearic acid and PAO were initially set up using the control setting from our research, which were then modified slightly as needed to obtain the required smoke yields. The machines, which were identical, were then operated for 100 hours on eight-hour daily, 40-hour weekly, schedules. Samples of the materials were collected into glass vials from the hot pots after approximately every 20 hours of operation, for future chemical analyses to determine whether decomposition, polymerization, or other changes occurred during this thermal "aging."

DOP and PAO were observed to have similar aging properties. Both remained clear for 10-20 hours of operation at temperature, and then exhibited a deepening honey color which turned to yellowish-brown after 100 hours. The isostearic acid, however, began to chemically attack brass parts used in the ATI machine hot pots. Within a few hours the liquid had turned greenish, and

within 10-20 hours a deep greenish-black color developed. At the end of 100 hours, the material was black and quite viscous, indicating that polymerization might have been catalyzed by iron and copper complexes that were taken into solution.

ATI engineers expressed an interest in experimenting with modified hot pots of stainless steel, glass, ceramic, or other inert construction, that could eliminate these corrosion problems. Such machine modifications might also reduce discoloration and sludging of DOP and other liquids used in the pots, thus increasing elapsed times to the accumulation of sludge, with required periodic maintenance, and requiring less frequent replacement of the material itself.

After the break-in period, our LAS-X and diluter systems were taken to the ATI factory for detailed measurements of the test smokes from the three machines. Trials were first run with the aged materials in the machines. The hot pots were then drained and refilled with fresh materials, and a second set of trials was run.

The new TDA-100 machines are designed around standard DOP specifications, and their operating temperatures are controlled by fixed-wattage heaters. Nevertheless, it was demonstrated that Army test specifications could be met with the new materials, without modification of the machines. ATI engineers indicated that if it were desired to deliver a new machine with, e.g., PAO instead of DOP, only a minor modification would be required to match the heater wattage to the proper operating temperature range of the replacement material, thus further improving the "monodispersity" of the of the test smoke.

After the machines were refilled with fresh materials, it was found that the specifications of the DOP and PAO smokes were very similar. Within the range of operating controls, the PAO smoke produced had a GMD of 0.22 μ m with a GSD of 1.29, while the DOP smoke, with optimum machine settings, had a GMD of 0.21 μ m with a GSD of 1.29. The fresh isostearic acid also was found to be able to produce a smoke that met Army specifications, within the available range of machine operating controls, but the latter material was not subjected to further detailed testing. Primarily because of its non-corrosiveness and better aging properties, PAO was selected as the tentative candidate of choice to replace DOP in existing Q-127 and new TDA-100 penetrometer machines with a minimum of downtime and machine modification.

Further testing at ATI with Emery 3004 allowed operators to become familiar with the range of TDA-100 adjustments and their interactions, so that smoke specifications were gradually improved using this new material. In most recent tests, Emery 3004 produced smokes with GSDs smaller than 1.25.

Recently manufacturers of PAOs¹³ including Emery 3004 have reissued MSDSs, as required by law when previously unknown but pertinent information becomes available, to reflect the 1982 findings of Guiney¹⁴ on the acute toxicity assessment of PAOs.

The new Emery MSDS for PAOs claim that although the toxicities estimated in Guiney's study were significant, the test conditions were such that the test animals (rats) were subjected to great physical insults,

sufficient that observed histopathical changes may have been a response to these insults rather than being related to a specific compound toxicity effect. The MSDS indicate that PAOs may be considered non-hazardous, for all practical purposes, by inhalation. Indeed all oils, including the purest of mineral oils, are capable of causing "oil pneumonia" and/or death by suffocation when inhaled at very high aerosol concentrations for periods of more than several minutes.

Since oils cannot be cleansed easily from the lungs due to their extreme hydrophobicity, and a build-up and coating of the lung surfaces is inevitable. Humans and animals subjected to such physiological insults respond by coughing, and by exiting the contaminated area. A confined test animal, on the other hand, would be subjected to great physical and psychological trauma in the presence of very high, suffocating oil aerosol concentrations, and could succumb rapidly for a variety of reasons.

To investigate the exact nature of conditions to which the test rats were subjected, visual and other data observations from Guiney's paper were analyzed using optical constants from a paper¹⁵ containing optical extinction (i.e., attenuation) coefficients at wavelengths including the visible, for oil smokes and aerosols. From the extinction coefficients, the actual oil aerosol concentrations to which the rats were subjected were calculated.

The test visibility conditions were such that the heads of the rats confined in test chambers could be seen under normal lighting conditions, but their hind quarters could not. This would be roughly equivalent to subjecting oneself to an oil aerosol or "fog" so thick that one could not see a hand six inches in front of his or her face. The aerosol mass concentration was estimated at 5,000 mg/m³ (5 g/m³), or roughly 1,000 times the PEL or TLV values normally given as safe for occupational exposure limits for oil mists.

Thus having established that significant chemical decomposition does not occur in Emery 3004 even when heated for more than 100 hours at high temperatures, this material was submitted for mutagenicity testing beginning with the Ames assay system. No mutagenic potential was found in this testing which was completed in August 1990. Emery 3004 is now undergoing the recessive sex-linked mutation study in fruit flies, and a contract is being negotiated to perform the micronucleus test in mice.

On March 15, 1991, a formal letter request was sent from the Chief of CRDEC's Health and Veterinary Services Office (HVS0), thru the Commander, U.S. Army Material Command, to the U.S. Army Surgeon General. The letter, SUBJECT: "Request for Approval of Emery 3004 as an Army-Wide Substitute Material for Dioctyl Phthalate (DOP)," included as enclosures an MSDS for Emery 3004, and a summary of mutagenicity testing. As of the writing of this report, an anticipated response concerning the question of approval from the Surgeon General has not been received. Meanwhile, we are performing preliminary air monitoring to determine potential worker exposure levels to Emery 3004, and to compare these to the OSHA Oil Mist Permissible limit of 5 mg/m³.

The worker exposure threat is greater from "hot smoke" machines than from machines that do not heat the smoke material, e.g., those generating "cold smokes" by spraying and other mechanical processing of the aerosol, rather than by using vaporization/recondensation techniques. Thus, approval from the Surgeon General to use Emery 3004 in hot smoke testing is tantamount to approval for its use in cold smoke testing as well, replacing less desirable materials such as corn oil or ordinary mineral oils.

Two cold smoke studies have been completed recently at CRDEC. Tests with a Laskin nozzle system, like that used in Army M-14 mask face fit penetrometers, showed that DOP produced aerosols with CMDs near 0.325 μm , while aerosols of Emery 3004 had CMDs near 0.295 μm under the same test conditions.

Other tests conducted during machine acceptance procedures of the new Los Alamos National Laboratory's High Flow Alternative Test System ("HIFATS") used materials other than DOP including Emery 3004 and another good CRDEC alternative material for DOP, "Emersol 875" (isostearic acid). We are now awaiting LANL's report of test results.

Collaborative cold smoke studies also are being conducted with the National Institute of Occupational Safety and Health (NIOSH). Comparisons of aerosols produced by the TSI Model 8110 filter tester using DOP, and several CRDEC-identified replacement materials, still are ongoing. DOP produces cold smokes in this tester that have particle size distributions and mass concentrations that are similar to those of CRDEC replacements including Emery 3004, Emersol 875, and a new material, "Emerest 2310" (isopropyl isostearate).

Thus, Emery 3004 has the potential to replace DOP in a great many hot and cold smoke testing applications.

5. CONCLUSIONS AND RECOMMENDATIONS

In summary, it would appear that the test conditions under which PAOs were considered to be potentially toxic by inhalation were completely unlike those reasonably expected to be found in actual experience. The acute toxicities of the PAOs are comparable to that of DOP. Since Emery 3004 presents no evidence of carcinogenicity,¹⁶ is not toxic under normal operating conditions, and can be used to replace the suspected carcinogen DOP directly in operating machines (with no mission interruption and while meeting or exceeding accepted Army filter test standards), it must be considered the prime candidate for approval as a DOP replacement by the U.S. Army Surgeon General

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